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## Formation of Silicate Grains in Circumstellar Environments: Experiment, Theory and Observations

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Amongst chemical reactions(1) in the molecular universe(2), condensation reaction is probably the most poorly understood. The condensation of a solid from its components in the gas phase occurs in many parts of our galaxy such as stellar mass outflows, the 'terrestrial' region of protoplanetary disks and in primordial solar nebula(3). But how does the transition occur from molecules to intermediate clusters to macroscopic grains? The major focus of the present work is the identification of chemical condensation reaction pathways that lead to the formation of stoichiometry, composition and crystallinity of cosmic silicates from vapor phase species.

O, Mg, Si, and Fe are the four major cosmically abundant mineral-forming elements(4). Are the initial magnesium-iron silicate condensates formed from the oxygen bearing gas phase species stoichiometric or an ill-defined assemblage of amorphous grains(5)? An answer to this fundamental question is a key step in the identification of chemical condensation pathways of specific molecule-solid transitions and elucidation of subsequent heterogeneous chemistry involving kinetics of gas-solid interactions(6).

It has long been advocated(7) that interstellar silicate grains are amorphous with non-stoichiometric elemental ratios and that circumstellar outflows(8), from evolved stars, are the primary contributors to transitions from molecules to such type of silicates. In contrast to the disordered compositions in silicates, recent infrared space observatory (ISO) observations(9) indicate an important fraction of interstellar silicates appear in crystalline form in the outflows of circumstellar shells of evolved late-type stars at low ambient color temperatures. The latest ISO observations(10) invariably indicate that most crystalline silicates are Mg-rich end members, for e.g. forsterite ( $\text{MgO}_2(\text{SiO}_2)$ ), and the Fe/Mg ratio is close to zero. Further, with the Mid-Infrared Interferometric Instrument (MIDI) installed at the Very Large Telescope Interferometer (VLTI), spatially resolved detections and compositional analyses of silicates in the inner-most two astronomical units of three protoplanetary

disks have finally been reported(11). It was observed(11) that silicates within the inner region of protoplanetary disks are highly crystallized, more so than any other dust observed in young stars until now. These observations(11) imply the role of vaporization and subsequent gas-phase condensation processes in the formation of crystalline silicates.

The 'nominal' molecules of observed crystalline silicates such as forsterite  $(\text{MgO})_2(\text{SiO}_2)$  do not exist in the gas phase(8). The growth of crystalline silicates occurs by heterogeneous chemistry in unique catalytically active pathways through gas-surface interactions at high temperatures. Thus one of the most fundamental questions in grain formation studies is which one among the high-temperature condensable gas-phase species is going to nucleate first at a significant condensation rate to provide a molecular surface (cluster) enabling condensed phase growth of minerals.

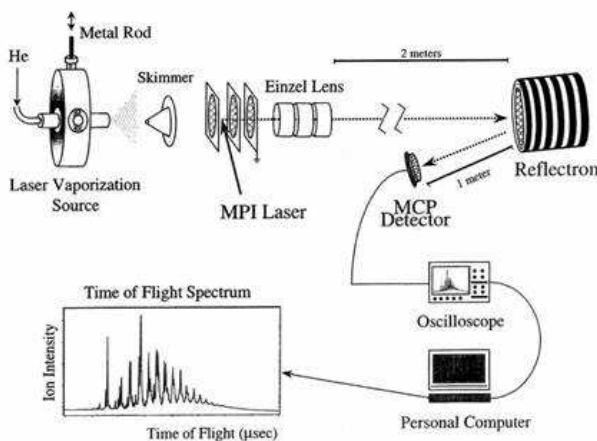
$\text{SiO}$  is one of the most abundant reacting oxygen bearing condensable gas-phase species in molecular astronomical regions. The current observational data(12) based on UKIRT indicate that  $\text{SiO}_2$  is a most plausible solid species contributing to the growth and evolution of various silicates seen in the infrared spectra of oxygen-rich evolved stars. Based on laboratory smoke condensation experiments and analysis of end products, it was conjectured(13) that silicate formation in the circumstellar envelopes surrounding M-type giants begins with the formation of pure  $\text{SiO}_x$  clusters. There are no direct and almost no experimental studies on the role of molecular processes on formation of silicates in high temperature clouds. In an attempt to resolve this critical question on the formation of  $\text{SiO}_x$  clusters as initiating condensation of cosmic silicates, we report for the first time, an experimental study of cluster intermediates and their growth during the condensation of a cosmically abundant molecular species silicon monoxide. In addition, first principles gradient corrected density-functional theoretical studies(14) have been carried on the geometry, electronic structure and stability of  $\text{SiO}_x$  clusters. It is shown that the synergistic approach(14) combining detailed experimental investigations on the clustering of  $\text{SiO}$  units in molecular beams and first principles electronic structure studies does elucidate the mechanism of condensation processes at the microscopic level that can lead to the formation of silicates on the one hand and silicon nanoparticles on the other.

## 1. Penn State Astrochemistry Laboratory

The schematic of the experimental set up is shown in Fig. 1. This set-up has been quite successful(15) previously for experiments ranging from intense pump-probe studies to basic photofragmentation processes, and a brief description of the apparatus follows. The surface of a rotating and translating quarter inch diameter silicon/silicon monoxide/silicon dioxide rod is ablated with the second harmonic of a Nd:YAG laser,  $\sim 4\text{mJ/pulse}$ , 8ns (532nm), at an adjustable time delay after which a pulsed valve is actuated. The species formed are quenched in a stream of buffer gas, and are further cooled by subsequent supersonic expansion through

a conical-shaped nozzle. Following expansion into vacuum, the supersonic jet, including both neutral and charged species, is skimmed as it enters the ionization chamber housing the high voltage time-of-flight (TOF) grids. The construction of geometry of this double acceleration region is based on the design of Wiley and McLaren(16). If the ionic species directly from the laser vaporization source are of interest, these species can be pulse extracted into this home built reflectron(17) time-of-flight mass spectrometer using two fast high-voltage transistor switches. This approach is quite straight forward in that the two TOF high voltage repeller and extractor grids (shown in Fig. 1) are initially kept at ground potential and then almost instantaneously ramped up to a higher voltage, resulting in the rapid acceleration of the ions toward the detector, after the ion packet has had the sufficient time to migrate down from the source. The ions of interest travel approximately three meters before reaching a multi-channel plate detector. By choosing appropriate decelerating and reflecting fields in the reflector, the larger initial kinetic energy distribution, compared to neutrals, can be further compensated.

Figure 1. Experimental Apparatus



To assess the neutral species distribution coming directly from the condensation source, the experimental set up is only slightly altered in that the TOF grids are now kept at a constant high voltage. Since the charged species are not able to penetrate the area between the acceleration grids, due to charge repulsion, the neutral species in the molecular beam are simply ionized and subsequently accelerated and detected. What makes our experimental setup somewhat unique is our ability to use a femtosecond laser for multiphoton ionization. By utilizing an ultrafast laser, all of the energy is delivered to the system of interest on a time scale that is much shorter than any relaxation pathway(18). In other words, the energy of the ultrafast laser pulse is delivered and absorbed before appreciable internal relaxation occurs. The multiphoton photoionization of neutrals is thus accomplished by focusing the output of a commercial Ti:Sapphire regenerative amplifier system. The 1-2 mJ/pulse, 50 fs, 800 nm laser pulse intersects the cluster beam perpendicularly between the previously mentioned extraction grids and thus provides nearly fragmentation-free ionization and detection of the neutral species in the molecular beam.

## 2. Results and Discussion

The ratio of oxygen to silicon in SiO is 1 while it is 2 for SiO<sub>2</sub>. One of the important astrophysical chemistry questions is whether the transition to SiO<sub>2</sub> occurs through the gradual oxygen enrichment of the agglomerated SiO units. It is also pertinent to ask if the origin of silicon nanoparticles currently believed to be the carrier of extended red emission(19) in diffuse interstellar medium is also rooted in the clustering of SiO units.

The time-of-flight multiphoton ionization mass spectra of neutral clusters formed by vaporizing solid SiO is not shown here, and the results would be published in the literature soon(14). Here we summarize our key findings. In addition to pure (SiO)<sub>n</sub><sup>+</sup> clusters, the spectra showed the presence of single oxygen enriched species namely Si<sub>2</sub>O<sub>3</sub><sup>+</sup>, Si<sub>3</sub>O<sub>4</sub><sup>+</sup>, Si<sub>4</sub>O<sub>5</sub><sup>+</sup>, Si<sub>5</sub>O<sub>6</sub><sup>+</sup>, Si<sub>6</sub>O<sub>7</sub><sup>+</sup> and small amount of Si<sub>7</sub>O<sub>8</sub><sup>+</sup>. There are variations in the intensity across each series. In the pure (SiO)<sub>n</sub><sup>+</sup> clusters, there is a precipitous drop in intensity from (SiO)<sub>5</sub><sup>+</sup> to (SiO)<sub>6</sub><sup>+</sup>. A similar decline in intensity is noticeable from Si<sub>6</sub>O<sub>7</sub><sup>+</sup> to Si<sub>7</sub>O<sub>8</sub><sup>+</sup>. In addition there is a large peak at Si<sup>+</sup>. The oxygen rich species Si<sub>2</sub>O<sub>3</sub><sup>+</sup> and Si<sub>3</sub>O<sub>4</sub><sup>+</sup> were also observed in the beams where clusters were formed through vaporization of silicon under oxygen or formed through the vaporization of solid SiO<sub>2</sub>, indicating that they are particularly stable. The most surprising experimental finding is the conspicuous absence of SiO<sub>2</sub><sup>+</sup> in all the experiments except for very minor intensity of the cations extracted from the silicon vaporized under oxygen. What processes then lead to the formation of observed oxygen enriched Si<sub>x</sub>O<sub>y</sub> species? Does SiO<sub>2</sub> form in this enrichment cycle? It is important to note that SiO<sub>2</sub> has the highest ionization potential of 12.19 eV of all the species. It would take at least 7 photons to ionize the clusters in our multiphoton ionization scheme. The lack of detection of SiO<sub>2</sub> is then simply related to the inability to ionize the species.

To delineate the molecular surface (cluster) enabling condensed phase growth of minerals, the first principles gradient corrected density-functional theoretical studies(14) have been undertaken. Recently, calculations have been carried out on the geometry, electronic structure and stability of oxygen enriched Si<sub>x</sub>O<sub>y</sub> clusters. It is found that the structures of the ground states of small Si<sub>x</sub>O<sub>x</sub> clusters containing up to 4 units are single rings. Si<sub>5</sub>O<sub>5</sub> is the smallest cluster where the Si-Si bond appears, and starting at this size, the elementary rings begin to assemble into multiple rings, that eventually lead to cages. It was found that the ground state structures at larger Si<sub>x</sub>O<sub>x</sub> cluster sizes have a natural tendency to segregate into pure Si cores with oxygen rich and particularly SiO<sub>2</sub> outer shells. To this end, we also investigated the stability of Si<sub>x</sub>O<sub>x-1</sub> and Si<sub>x</sub>O<sub>x+1</sub> species. The density-functional theoretical studies also show that successive collisions of any oxygen enriched Si<sub>x</sub>O<sub>x+1</sub> species with a substrate cluster Si<sub>x</sub>O<sub>x</sub> (n>5) would lose an SiO unit in each collision and thus providing a microscopic mechanism to the formation of SiO<sub>2</sub> as the terminal member. The observed intensity distribution of Si<sub>6</sub>O<sub>7</sub>, Si<sub>5</sub>O<sub>6</sub>, Si<sub>4</sub>O<sub>5</sub>, Si<sub>3</sub>O<sub>4</sub>, Si<sub>2</sub>O<sub>3</sub> in the mass spectra are completely consistent with the above pathway through reaction cascades. The observed anomalous compositions in Si<sub>x</sub>O<sub>y</sub> clusters and their formation kinetics must be taken into account, prior to a mechanism is being invoked or an argument is presented against the role of SiO molecules

in chemical models of formation of circumstellar silicates(13; 20).

In our laboratory we intend to make measurements on the vibronic structure of observed compositions of silicon oxide clusters  $\text{Si}_x\text{O}_y$  in the size distribution between two and maximum of twenty atoms. The interpretation of optical spectra would need a close interaction between experiment and ab initio quantum chemical calculations of polyatomic molecules. In the second part of our experimental studies we tend to bring our expertise of real time pump-probe studies(15) of cluster reactions to measure the dissociation ofate (lifetimes(5)) of 'activated complexes' - the reverse process of recombination reactions (and/or disproportionations to products through low-energy exit channel, if any) using femtosecond ultrafast laser pulses. The measured data on lifetimes of collision-complexes coupled with information in energetics of clusters are then incorporated into the rate expression of microcanonical transition state theory(21) to yield cross sections for the reactions between relevant clusters to elucidate the microscopic condensation rates.

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